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Improving the Analytical Accuracy of Electron Spin Resonance Spectrometry

Technical Report No. 10

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Ira B. Goldberg

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Sources of error in Analytical Electron Spin Resonance Spectrometry are discussed. Errors due to gain of the lock in amplifiers and modulation amplitude settings can be reduced if the settings are properly calibrated or if the attenuators are rebuilt. It is also necessary that the incident microwave power level is monitored and that the cavity is reproducibly tuned. A method of correction for incomplete integration of Lorentzian lines is discussed.

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INTRODUCTION

Several reports (1-5) addressed the effects of instrumental parameters of electron spin resonance (ESR) spectrometers on the accuracy and precision of analytical determinations. Warren and Fitzgerald (2) carried out a systematic statistical evaluation of both instrumental and sampling parameters, and located many sources of random scattering of data. Nevertheless, the origin of some of these errors have not been elucidated with respect to improving the overall performance of analytical ESR spectroscopy.

Recently, we interfaced out ESR spectrometer to a laboratory computer (6) in order to study transient species as well as to carry out data reduction for analytical measurements. This has enabled us to examine the effect of instrumental parameters in a similar way to Warren and Fitzgerald (2), but with greater precision. From these experiments, we were able to determine several modifications to the instrument and to the operating procedure so that optimum performance of the instrument can be obtained. In this report, the causes of these instrumental errors are discussed, and steps are recommended to overcome these problems. These include the gain of the lock in amplifiers, modulation amplitude control, incident power level, and cavity tuning. Although our own instrument is a highly modified Varian V-4502 spectrometer, our results are generally applicable. Because many reported analytical measurements were carried out on the E-3 spectrometer (1-5), some of our results will be directed to that instrument.

EXPERIMENTAL SECTION

All measurements reported here were carried out on a modified Varian V-4502 ESR spectrometer with a dedicated PDP 8/m computer (6). The microwave power was monitored with a General Microwave, Model 476 power meter. Double

integrations were carried out subsequent to the experiments and corrected for finite integration length according to the method described in the appendix. Peak-to-peak amplitudes were measured as the difference between the maximum and minimum voltages of the digital spectrum and is accurate to ±0.005V relative to a maximum range of +5 to -5V. Measurements of the modulation amplitude were also carried out as previously described (5) for our V-4502 spectrometer as well as two E-9 and two E-3 spectrometers.

RESULTS AND DISCUSSION

<u>Signal Level:</u> The output signal amplitude of the lock in amplifier is determined either by using a resistive divider to attenuate the signal, or to change the gain of one of the amplification stages prior to the output. For a signal divider, such as shown in Fig. 1, the attenuated voltage V_i divided by the signal input V_s into the attenuator, is given by equqtion 1.

$$f = \frac{V_i}{V_s} = \frac{\sum_{i=1}^{n} R_i}{\sum_{j=1}^{N} R_j} \tag{1}$$

where the attenuated signal is measured across resistors i = 1 to n and the input signal is across resistors i = 1 to N. Given that resistors of a specified uncertainty, δR, are used, the error in the value of V_i/V_s is determined by the sum of the squares of the partial derivatives of V_i/V_s with respect to R_i's and R_j's (7). The result of this operation is

$$\frac{\delta(1/f)}{1/f} = \left\{ \frac{1}{\left(\sum_{i=1}^{n} R_i\right)^2} \cdot \left[\left(1 - \frac{1}{f}\right)^2 \sum_{i=1}^{n} (\delta R_i)^2 + \sum_{j=1}^{N} (\delta R_j)^2 \right] \right\}^{1/2} \tag{2}$$

where $\delta(1/f)/(1/f)$ is equal to the relative error in the attenuation. For the Varian E-3, E-line series and V-4500 series spectrometers, this attenuator consists of two divider networks as shown in Fig. 1. Divider 1 provides steps of 25% in the attenuation while Divider 2 provides steps of a factor of 10. In the 100 KHz phase sensitive detectors of both the E-3 and V-4502 spectrometers, divider 1 is constructed of resistors of ±5% tolerance while divider 2 is constructed of resistors of ±1% tolerance. Both dividers on the E-line series are constructed of resistors of ±1% tolerance.

The effect of this design is shown in Table 1 for the E-3 spectrometer. Note that the gain indicated on the spectrometer and the gain calculated from the resistors deviate by as much as 5% (e.g., the indicated value of 1.25 is actually 1.31), and the uncertainty increases as the attenuation increases as predicted by Eq. 2. The situation is similar for the V-4502. We have investigated the gains on the V-4502 spectrometer utilizing actual ESR samples, a small 100 KHz voltage input to the phase sensitive detector, and a small DC voltage across the attenuator and find deviations of the magnitudes predicted by equations 1 and 2.

Divider 2 of the E-3 spectrometer has five gain settings. Those of 10^2, 10^3 and 10^4 consist of three resistors shunted by the total resistance of divider 1. The gain settings of 10^5 and 10^6 alter the feedback loop of an amplifier. Thus, the three greatest amplifications contain a systematic error of ±3.5% determined principally by the total resistance of divider 1 and by the uncertainty of the feedback resistors.

The E-line series contains resistors of ±1% tolerance and is therefore more precise than either the V-4502 or E-3 spectrometers.

There are several solutions to correct for the uncertainty of the attenuation: the attentuator can either be calibrated or it can be rebuilt using

trimming resistors to make the attenuation values agree with the indicated values. We have chosen the latter approach since our instrument is used by a number of different people.

Modulation Amplitude: The modulation amplitude of the spectrometer is controlled through a resistive network similar to the signal level dividers. In addition the power of the output amplifier is directed into a low impedance 8Ω or 32Ω load. As a result there can be uncertainties in the modulation amplitude at the sample caused by the errors in the divider network as well as non-linearities at high modulation amplitude output powers.

The divider network for the divider 1 of the E-3, V-4502, and E-line spectrometers are identical to that of the signal level control shown in Fig. 1. Divider 2, which permits steps of 0.01, 0.1, 1.0, and 10 Gauss, is constructed of four resistors of ±1% tolerance. Errors for these are shown on Table 1 for the E-3 spectrometer. Similar results are obtained for the V-4502 spectrometer. The modulation amplitude attenuator of the newer E-line series is constructed from 1% resistors, and is thus subject to less uncertainty. As before, these errors can be rectified by proper calibration techniques or reconstruction. Since only relative values are important, calibration can be carried out on a sample with a linewidth much greater than the maximum modulation amplitude, such as $MnSO_4$, such that the signal amplitude is linear with the modulation amplitude.

At modulation amplitudes greater than about 20 Oe, loading of the output amplifier can also contribute to deviations between the indicated and actual values. Randolph (8) has shown that the double integral of the ESR signal is proportional to the modulation amplitude. However, the amplitude of the derivative signal is only linear when the peak-to-peak modulation amplitude, H_m,

is less than about 0.2 times the derivative peak-to-peak linewidth (9,10). At these values of H_m the sensitivity of the ESR spectrometer is much lower than optimum, such that higher modulation amplitudes are required for analysis of lower concentrations. Thus, in order to realize the full dynamic range of ESR, it may be necessary to calibrate at least the relative values of the higher modulation amplitudes. On the V-4502 spectrometer, we find that H_m is linear with the indicated value to 2500 "units" which corresponds to 12.5 Oe. Between 2500 "units" and 8000 "units", H_m is lower than expected, falling off to 29 Oe instead of the anticipated 40 Oe (11). At these high amplitudes, the waveform also becomes distorted.

Power Level: On the E-3, E-4 and V-4500 spectrometers, the power level is determined by a vane or flap attenuator in which a lossy material is inserted into the waveguide. The maximum accuracy of these attenuators is ±0.5 db to about 40 db and ±1db to about 60 db. The reproducibility is only slightly better. Thus, depending on the range of attenuation this can amount to a ±6% to ±12% error in the power level. The rotary vane attenuators used in the E-line series offer slightly greater accuracy but much greater reproducibility. Nevertheless, it is advisable to utilize a power meter to monitor the incident power to the cavity. These are reproducible to ±0.5% and accurate to ±1%. This permits materials which require different incident powers to be compared to any given standard. We make the assumption here that the cavity tuning remains fixed as does the bias level to the detector.

Cavity Tuning: One of the most critical aspects of reproducible ESR determinations is that the cavity is reproducibly tuned. In addition, the detector should be biassed at the same operating point. Often, once the microwave power is determined, the iris on the cavity is adjusted such that the

detector is biassed at the same current level for all measurements. This however precludes the cavity being tuned in a reproducible manner. Alternatively, microwave power can be supplied to the detector in which this biasing radiation is in phase with the radiation reflected from the microwave cavity. This permits the cavity to be maintained near critical coupling which is the most sensitive and most reproducibly set point. Results of these methods are illustrated in Fig. 2. At incident powers greater than about 10mW (c.a. 17 db), the point of critical coupling is very close to the point at which sufficient power is reflected to properly bias the detector, and the ESR performance is equal to that of the method of external biassing. Below that value, the cavity iris must be opened which decreases the power density at the sample. Thus, the value of $A/P^{\frac{1}{2}}$, where A is the peak to peak amplitude of the derivative of the absorption and P is the incident power, decreases as the attenuation is increased. If biassing is carried out using an external arrangement, such as provided on the E-line series spectrometers, the value of $A/P^{\frac{1}{2}}$ remains constant as long as the resonance transition is not saturated. A plot of log A vs log P, for a sample of powdered $MnSO_4 \cdot H_2O$ gave a least-squares slope of 0.503±0.006 over range of 60 db attenuation.

The results shown here agree with those presented by Warren and Fitzgerald (2), and explain some of the errors of ESR determinations. High precision can be obtained if the properties of the detection system and microwave cavity are taken into consideration. As others have concluded (2,4), changing the modulation amplitude introduces additional uncertainty into the measurements. However, this uncertainty is not so great if the modulation amplitude is calibrated and the non-linearity of the peak-to-peak amplitude with modulation amplitude is taken into account (1,5), or if the double integral is used as a

measure of concentration (1,5,8). We assume that the samples are not saturated by high incident powers (12), and that the cavity is not loaded by excessive material (13).

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Table I

Factors for Signal Level and Modulation Amplitude[a] and
Uncertainties Associated with These Factors for an E-3 Spectrometer

indicated gain	theoretical[c] gain	uncertainty[d] (%)	attentuation factor
	Signal Level and Modulation		
0.5	0.509	4.7	0.13
0.63	0.608	4.0	0.15
0.8	0.808	3.2	0.20
1.0	1.007	2.7	0.25
1.25	1.307	2.3	0.33
1.6	1.606	2.1	0.40
2.0	1.995	1.8	0.50
2.5	2.504	1.5	0.63
3.2	3.182	1.1	0.80
4.0	4.000	0.0	1.00
	Signal Level		
1.0×10^{2}	1.003×10^{2}	1.3	0.01
1.0×10^{3}	0.990×10^{3}	1.1	0.1
1.0×10^{4}	1.008×10^{4}	3.5[b]	1.0
1.0×10^{5}	1.017×10^{5}	3.5+1.0[b]	10.
1.0×10^{6}	1.047×10^{6}	3.5+0.9[b]	100.
	Modulation Amplitude		
0.01	0.01003	1.3	1.0×10^{-3}
0.1	0.0990	1.3	1.0×10^{-2}
1.0	1.008	3.6	1.0×10^{-1}
10.0	10.00	0.0	1.0

[a] determined from E-3 schematics

[b] for these two settings, 3.5% represents a systematic error

[c] calculated from equation 1

[d] calculation from equation 2

Appendix 1. Double Integration of the Derivative of Lorentzian Absorption Lines

The derivative of Lorentzian absorption lines, normalized to unity, is described by equation A-1 (14)

$$Y' = \frac{1}{\pi\Gamma} \cdot \frac{2\Gamma^2 (H-H_o)}{[\Gamma^2 + (H-H_o)^2]^2} \qquad \text{(A-1)}$$

where H is the applied magnetic field, H_o is the magnetic field at resonance and Γ is the half-width of the absorption at half-height. The double integral of this lineshape between the points H_o-H_a and H_o+H_a is then given by

$$I = \int_{H_o-H_a}^{H_o+H_a} \int_{H_o-H_a}^{H} Y'dH'dH = \frac{2}{\pi}\left\{\tan^{-1}\left[\frac{(H_o-H_a)}{\Gamma}\right] - \frac{\frac{(H_i-H_a)}{\Gamma}}{1+\left(\frac{H_o-H_a}{\Gamma}\right)^2}\right\} \qquad \text{(A-2)}$$

Assuming that $\Delta H_{pp} = \frac{\sqrt{2}}{3}$, and dividing the experimentally determined double integral by I, gives the value of the double integral which would be obtained if an infinite scan could be used.

The computer program used for integration defines the field at maximum absorption and computes the peak to peak width. Magnetic fields equidistant from the absorption maximum are then defined, and the zero-derivative point is determined. Double integration is then carried out by Simpson's rule, and the correction factor described by equation A-2 is then applied to the results. A series of twenty experiments on a sample of $MnSO_4 \cdot H_2O$ yielded a standard deviation of 0.6% of the mean value.

This approach can also be used for multiple overlapping lines. Typically, only the outermost lines need to be treated. Because many lines are contained in the spectrum, small errors in the correction factor do not greatly influence the final result.

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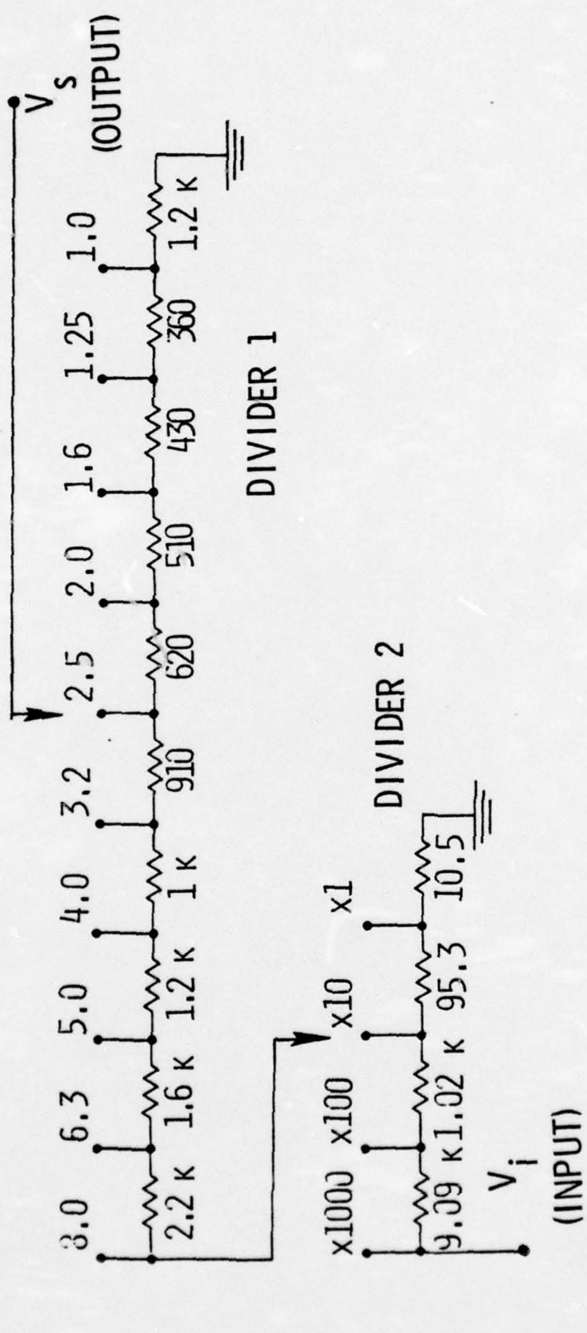
Figure 1. Schematic representation of the attenuator used in the V-4502 ESR spectrometer to control the output signal level and modulation amplitude of the 100 KHz phase sensitive detector. Resistance values are given below the resistor in ohms, and the attenuation normalized to a value of 8000 is given adjacent to the contact points.

Figure 2. The ESR signal for strong pitch divided by the square root of the power incident to the microwave power vs the attenuation of microwave power. 0 db corresponds to 580 mW. Power saturation of the sample begins at attenuations small than 20 db.


8.0
6.3
5.0
4.0
3.2
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2.0
1.6
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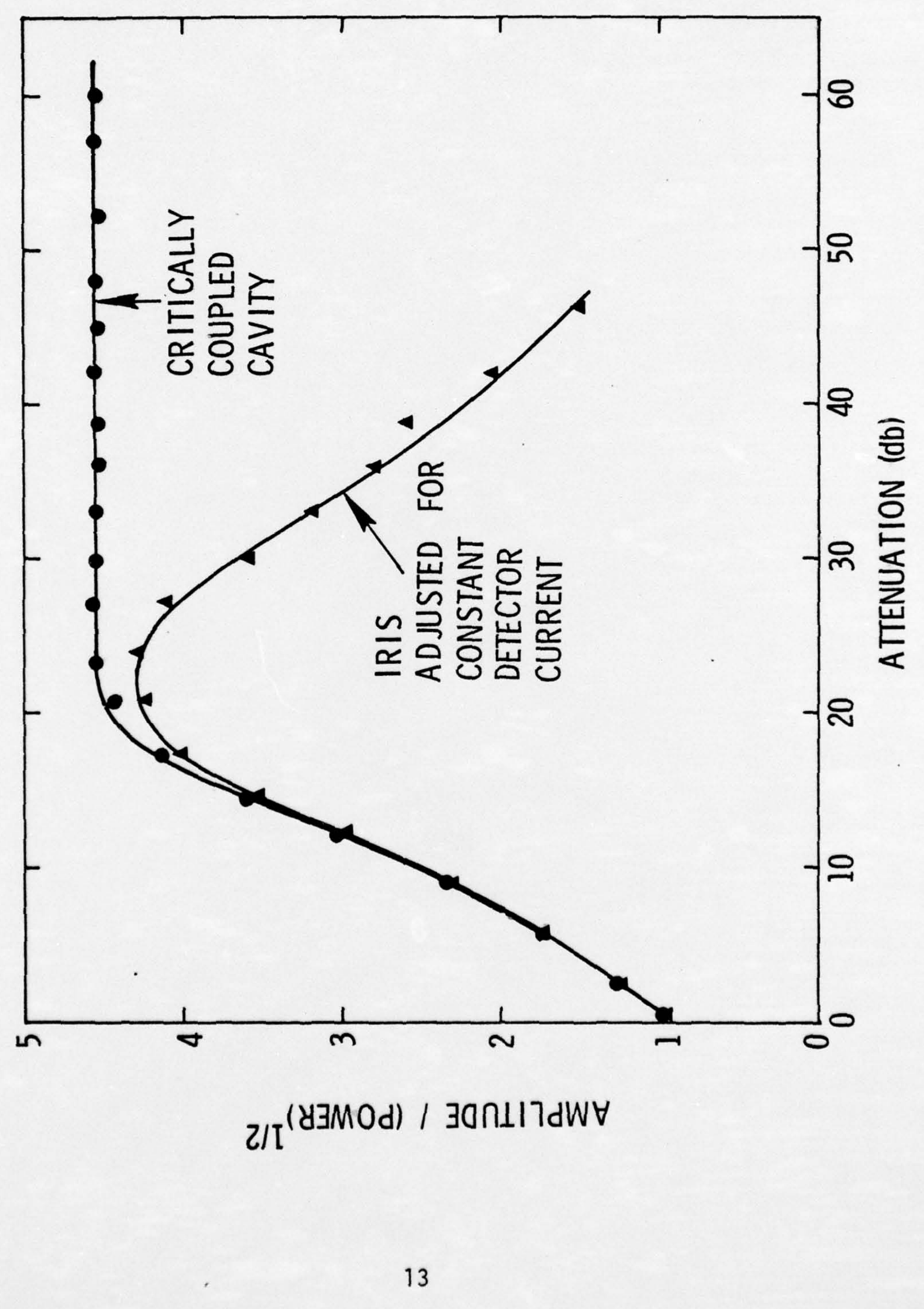
V_s
(OUTPUT)
2.2 K
1.6 K
1.2 K
1 K
910
620
510
430
360
1.2 K
DIVIDER 1
DIVIDER 2
x1000
x100
x10
x1
1.02 K
95.3
10.5
V_i
(INPUT)

Figure 1


CRITICALLY
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0
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20
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60
0
1
2
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Figure 2

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